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(54) **Fatty ethenoid acylaminoorganosilicon compounds and their use in compositions for coating glass.**

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**EP-A- 0 136 680
FR-A- 1 578 807
FR-A- 2 178 704
US-A- 4 130 677**

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Description

The instant invention relates to the use of acylaminoorganosilicon compounds in compositions to enhance the surface properties of glass articles with the exception of glass fibers.

In US-A-2,929,829 and 2,928,858 Acylaminoorganosilicon compounds are described. These acylaminoorganosilicon compounds were considered useful as, among other things, acid-base indicators; additives for silicon products, such as oils and gums; thermosetting resins for coating materials; and ultraviolet ray absorbers.

Subsequent to said work, improvements based on acylaminoorganosilicon compounds were discovered.

In U.S.-A- 3,249,461, the use of conjugated olefin containing acylaminoorganosilicon compounds was taught as effective fiber glass reinforcing agents. In U.S. - A - 3,681,266, a distinct class of acylaminoorganosilicon compounds was fluorine modified to provide a coating material that is useful as a water repellent. In U.S. - A - 3,720,699, a new and useful class of haloorganoacylaminoorganosilicon compounds are reported to be useful as a coating material.

A variance on the theme, U.S. - A - 3,755,354 is directed to amide acid and imido-substituted organosilicon compounds that are reportedly useful as glass fiber coupling agents. In a closely related U.S. - A - 3,787,439, imido-substituted organopolysiloxanes were disclosed, including conjugated, unsaturated acylaminoorganosilicon compounds, as additives for glass fibers.

In U.S. - A - 3,959,327, acylaminoorganosilicon compounds with thio-containing substituents were reported as plasticizers and coupling agents.

A new class of complex acylaminoorganosilicon compounds was reported in U.S. - A - 4,209,455 and 4,284,548. In each the mono- and bis-silanes were characterized by a single acylamino group and at least one secondary or tertiary aminoorgano group. These compositions were considered useful in fiber sizes.

In U.S. - A - 3,746,738, acylaminoorganosilicon compounds that contained various pendant silanes were described as useful glass fiber sizes.

In U.S. - A - 3,537,832, silylated polymers were prepared by amidation of acid chloride modified polymers with aminoorganosilanes for use as coating materials.

CA 84:59633W teaches stearoyl and oleoyl acylaminoorganosilicon compounds.

In EP-0 136 680, filed on 28.9.1984 and claiming a priority of 30.9.83 acylaminoorganosilicon compounds containing fatty ethenoid groups are described as useful glass fiber sizes.

It is well known in the art that glass derives its strength from an unblemished surface and any scratches or flaws which are present on the surface decreases the strength of the glass many-fold. Glass articles, such as bottles, sheets and fibers possess their maximum strength shortly after they are formed. Their strength rapidly diminishes when they are subjected to abrasive contact in the course of handling, packaging and shipping.

This problem is illustrated for glass containers that are used by processors of food and beverages. The glass containers are subjected to a number of processing operations. The containers are washed, filled, closed, labelled and packaged for delivery. During these operations, the glass containers are rubbed or otherwise contacted in various ways, often under high pressure, which can cause scratching. The glass containers repeatedly come into contact with each other as they move from station to station and during the various washing, filling, closing and packaging operations. Although the need for a glass protective coating was described for glass containers, there are other applications in which this coating for glass articles will be useful.

Numerous references to compositions and materials used as protective coatings exist in the patent literature for glass surfaces. The most widely used protective coatings, for glass bottles, include tin and titanium compounds such as titanium and stannic halides and alkyl titanates. These materials are sprayed on the surface of the glass at a temperature of from 480°C to 640°C. The tin and titanium compounds are believed to react with moisture in the air to form a TiO₂ or SnO₂ layer. After the glass is annealed to about 230°C or lower, a second coating that consists of a polyethylene emulsion, is applied as described in U.S. - A - 2,995,533, 3,598,632, 3,496,825, 3,853,612 and 4,272,587. The coating system described in these patents provide a very good protective finish to the glass surface. The coating, however, is very expensive. The price of the intermediates, such as the stannic halide or titanium compounds, the two step application, and the damage to the metal equipment resulting from the corrosive nature of the metal halides all contribute to the unit cost of this coating.

Protective aqueous coating compositions consisting of an organofunctional silane and an organic polymer, such as, for example, vinyl polymers (U.S. Patent No. 3,998,985), polyamino-acrylate esters (U.S. - A - 4,224,365 and 4,250,068) and epoxy (U.S. - A - 4,056,208, EP - A1 - 57 595) are either difficult to apply, i.e. require a primer coat, costly or do not possess the combination of properties required for the glass

application, such as for bottles.

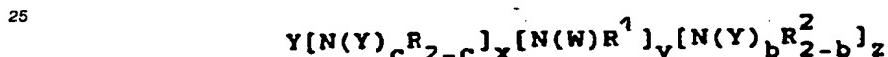
Attempts to circumvent the above problems consisted of coating the glass surfaces with an aqueous emulsion of an olefin such as polyethylene and a silane, such as polyethylenaminepropyltrimethoxysilane or an ethylenediaminopropyltrialkoxysilanes, (U.S. - A - 3,873,353) or a alkyltrialkoxysilane, (U.S. - A - 3,801,361) or gamma-aminopropyltriethoxysilane, (U.S. - A - 4,130,677) or simply an aqueous solution of a silane and an amine salt of acetic acid, (U.S. - A - 3,438,801). While good abrasion resistance and "labelability" are alleged for these coatings, the adhesion of the coating to the bottle when subjected to an aqueous wash, especially aqueous caustic wash, is too low for certain applications.

It is an object of this invention that special acylaminoorganosilicon compounds together with a dispersing agent and a fatty acid and optionally a polymer in combination with an aqueous emulsion of organic polymer, or with an organic solvent and/or water is used as coating composition to yield improved balance between the various glass surface properties, including labelability, appearance, abrasion resistance (wet/dry scratch), lubricity and durability to caustic wash over existing coatings that contain an organofunctional silane; the coating compositions do not generate toxic, corrosive or obnoxious fumes.

In accordance with the present invention, coating compositions for glass articles, as defined in claim 1 are provided.

DETAILED DESCRIPTION OF THE INVENTION

The fatty ethenoid acylaminoorganosilicon compounds represented by formula I above can be prepared by a variety of known techniques. The basic reaction is the acylation of an aminoorganosilane by reaction with a carboxylic organic acid, a carboxylic organic acid halide, an ester or anhydride derivative of a carboxylic organic acid. The aminoorganosilanes suitable for acylation are represented by the formula:



wherein Y and W are as defined in claim 1 but excluding



and X, R, R¹, R², b, c, x, y and z are as defined in claim 1. At least one Y must be $-R^5Si(OR^6)_{3-a}(R^7)_a$ and at least one other Y must be hydrogen.

Preferably, the aminoorganosilanes are such that R and R¹ are ethylene or propylene, R² is methyl or hydrogen, R⁵ is propylene, R⁶ and R⁷ are methyl or ethyl, a=0 or 1, b=0 or 1, c=1, x=1 to 4, y=0 to 3 and z=0 or 1.

Suitable acylation reagents are those represented by the general formula



where R⁴ is a monovalent hydrocarbon group containing anywhere from 8 to 24 carbon atoms and at least one double bond and X is a halogen atom, a hydroxyl group, an ester group (-OR⁸) or an anhydride group (-OCOR⁹). Wherein R⁸ and R⁹ are monovalent hydrocarbon groups.

The free fatty acid is converted to the acylation reagents by well known techniques. For instance, when X is to be halogen, the fatty acid is converted at room temperature or higher by simple addition of thionyl halide to the fatty acid and thereafter removal of sulfur dioxide and hydrogen chloride is effected. If an fatty acid ester is desired, it is obtained by catalyzed esterification with alcohols and fatty acid and removal of byproduct water. If the anhydride derivative is desired the anhydride derivative is produced by catalyzed dehydration of the fatty acid. Most, if not all, of these acylation reagents are commercially available.

The details as to the acylation reaction conditions between the monoprimary and/or secondary aminosilane and the carboxylic organic acid or derivative are more fully set forth in U.S. - A - 2,929,829

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where monoaminoorganosilicon compounds are reacted with carboxylic organic acid halides, a tertiary alkyl amine, such as Et₃N or pyridine may be employed to remove the HX and aid the completion of the acylaminoorganosilicon compound. In other instances an excess of aminoorganosilicon compound instead of the tertiary alkyl amine or pyridine is used to produce a mixture of aminoorganosilicon hydrogen halide and the corresponding fatty ethenoid acylaminoorganosilicon compound. In this latter approach the aminoorganosilicon hydrogen halide compounds remain as a water compatible co-reactive silane component which in some instances may provide a substantial benefit to end use handling and performance of the coating for glass articles.

For many coating applications it is preferred to use carboxylic acid chloride acylating reagents because they are readily available, highly reactive and least complicated by undesirable side reactions. Optional removal of HCl is sometimes advantageous.

Aminoorganosilanes having 2 or more amino groups and one or more silane groups are reacted with carboxylic organic acid halide to obtain a fatty ethenoid acylaminoorganosilicon compound which can have a combination of fatty acylamino, free amino and amine hydrogen halide groups as well as one or more silane groups.

Once again, reference is made to U.S. - A - 2.929.829 for particulars relative to reaction conditions.

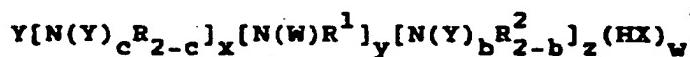
For production of water dilutable coatings from polyaminoorgano(poly)silanes, it is preferred to add carboxylic acid chloride slowly to a well stirred solution of silane in methanol, ethanol or the like at from 0° to 150°C preferably 25-70°C. The in situ formation of aminoorgano hydrogen halide salt groups which occurs during this reaction provides the product with water solubility or dispersibility. This preferred process for fatty ethenoid acylated derivatives of polyaminoorgano(poly) silane compounds generally is used to produce the same molar concentration of acylated amine and amine hydrogen halide salt groups. The molar concentration of free amino groups will largely depend on the extent of acylation initially undertaken in this process and can vary widely.

The compounds used according to this invention are complex structures, but can be produced by alternate methods. In one such method a polyalkyleneamine is reacted with the carboxylic organic acid, its acid halide or anhydride to provide a partial acylamino derivative, which is also an amino containing intermediate that is subsequently silylated by conventional means to provide the acylaminoorganosilicon compound desired.

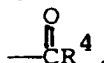
This process has a tendency to produce higher viscosity products with varying amounts of polysiloxane product in place of the full amount of silane ester groups. Subsequent dilute aqueous dispersions also show a somewhat greater tendency to destabilize with time.

In general, it is preferred to silylate polyalkyleneamines according to the teachings of U.S. - A - 3,746,738 and to subsequently acylate as previously described.

In all of the reactions set forth above the desired end product is a fatty ethenoid acylaminoorganosilicon compound represented by the general formula:



Preferably, the fatty ethenoid acyl aminoorganosilicon compounds are such that R and R¹ are alkylene radicals and more preferably ethylene or propylene. R² is methyl or hydrogen, R⁴ is a hydrocarbon radical containing 8 to 24 carbon atoms and at least one double bond, R⁵ is propylene, R⁶ and R⁷ are methyl or ethyl, a=0 or 1, b=0 or 1, c=1 to 4, x=0 to 3 and z=0 or 1, and at least one Y is -R⁵Si(OR⁶)_{3-a}(R⁷)_a and at least one other Y is



Exemplary of the fatty ethenoid acylaminoorganosilicon compounds are set forth in Table I below:

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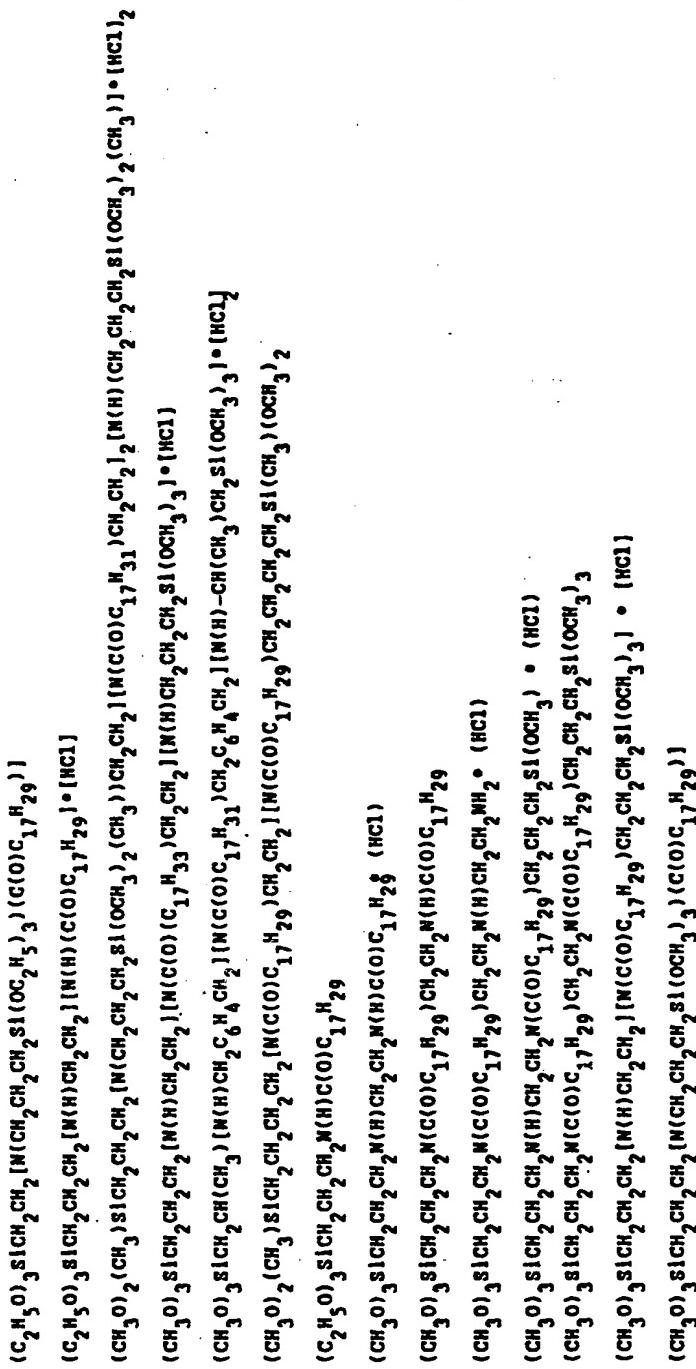
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TABLE I



The fatty ethenoid acylaminoorganosilicon compounds is used in combination with a dispersing agent,
 55 such as, an organic solvent and/or water. The organic solvent can be any of those commonly used to dissolve or disperse organic coatings, including alcohols, ketones, esters, ethers and the like. These solvents are useful as a vehicle for applying the fatty ethenoid acylaminoorganosilicon compounds to the glass surface. A preferred composition comprises from 0.01 to 20 weight percent of the fatty ethenoid

acylaminoorganosilicon compounds dissolved or dispersed into water. As prepared, it may be applied as hereinafter described. It is an aspect of the instant invention to use a three component coating composition as claimed in claim 13.

The organic polymer that can be used in combination with the fatty ethenoid acylaminoorganosilicon compounds can be a polyolefin including polyethylene, polypropylene; polyisobutylene; a polyether including polyethylene oxide, polypropylene oxide, and polyethylene oxide polypropylene oxide copolymer; and an epoxy or other polymer that imparts a waxy nature to the coating. A preferred composition comprises forming an aqueous emulsion of the polyolefin. Details for preparing this preferred emulsion are set forth in U.S. - A - 2,995,533.

10 The fatty acids that can be used in combination with the fatty ethenoid acylaminoorganosilicon compounds are principally derived from the body fat of animals, such as lard and tallow; from fruit pulp, such as palm and olive; the seed of plants, such as cottonseed, peanut, corn, safflower, sesame, sunflower, rapeseed, mustardseed, soybean and linseed.

It should not be construed to mean the acids are derived solely from non-petroleum materials.

15 Preferably, the fatty acid contains 8 to 18 carbon atoms: more preferably the fatty acids are stearic acid, oleic acid and/or linolenic acid.

The coating composition for glass articles is prepared by dissolving from 0.01 to 20 weight percent fatty ethenoid acylaminoorganosilicon compounds into water and then dissolving, dispersing or emulsifying from 0.01 to 50 weight percent fatty acid and optionally polymer.

20 Preferably, the coating for glass articles is prepared by dissolving from 0.05 to 3 weight percent fatty ethenoid acylaminoorganosilicon compounds into water and then adding 0.05-to-5-weight-percent-polyolefin in the form of an aqueous emulsion, as described in U.S.-A-2,995,533.

Another aspect of the instant invention is a two step coating process for glass articles in which 0.01 to 20 weight percent solution of fatty ethenoid acylaminoorganosilicon compounds is deposited into the glass 25 surface in one application step followed by depositing the fatty acid and optionally the polymer in a subsequent application step.

In the first application step, the fatty ethenoid acylaminoorganosilicon compounds are deposited from an aqueous or organic solution. The organic solvents can be any of those commonly used to dissolve or disperse organic coatings, including alcohols, ketones, esters, ethers, and so on. These solvents are useful 30 as a vehicle for applying the class of fatty ethenoid acylaminoorganosilicon compounds to the glass surface. A preferred composition comprises from 0.05 to 3 weight percent of the fatty ethenoid acylaminoorganosilicon compound dissolved into water.

In the second application step, the organic polymer that is dispersed in an organic solvent and/or water can be a polyolefin including polyethylene; polypropylene; polyisobutylene; a polyether including polyethylene oxide, polypropylene oxide, polyethylene oxide polypropyleneoxide copolymer; and an epoxy or other polymer that imparts a waxy nature to the coating.

35 Preferably, the organic polymer is applied as an aqueous emulsion of from 0.05 to 5 weight percent polyethylene, as described in U.S. - A - No. 2,995,533.

The fatty acids that can be deposited on the glass surface in the second application step are the same 40 as those which have been previously described.

The coatings for glass articles described in the instant invention can be applied by any techniques commonly known in the art of coatings including spraying, dipping, wiping, brushing and misting.

A preferable method for applying the coatings is to spray a solution of the coatings described in the instant invention onto a glass surface that is at a temperature between 90°C and 250°C.

45 Although not wishing to be bound by any specific limits on the amount of coating necessary to enhance the surface properties of the glass articles, it is advisable to employ at least 0.1 mg of the coating per cm² of the surface area of the glass article, with approximately 1.5 mg coating/cm² being preferred. It should be noted that at the lower coating levels, higher concentrations of the fatty ethenoid acylaminoorganosilicon compound is recommended if a two or three component coating system is employed.

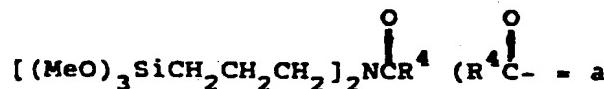
50 The following specific examples illustrate certain aspects of the present invention and, more particularly, point out methods of evaluating the same. All parts and percentages are by weight unless otherwise specified. For the purposes of these examples Me denotes a methyl group.

Production of Fatty Ethenoid Acylaminoorgano Compounds:

A.) Into a 1 liter, 3-necked flask equipped with dropping funnel, thermometer, thermosensor, mechanical stirrer, heating mantle, 324 mm (1 foot 3/4") O.D. Vigreux column, distillation head and receiver was charged 85.3 g (0.25 moles) of [(MeO)₃SiCH₂CH₂CH₂]₂NH, 35.4 g (0.35 moles) of triethylamine and 194.5 g of toluene. Starting at room temperature, through the dropping funnel was added to the stirred mixture 74.2 g , (0.25 moles)of linseed acid chloride. An exotherm resulted throughout the addition and

the reaction mixture temperature was held between 30° and 50° C by external application of a water/ice bath. After an additional hour of stirring at ~35° C the total reaction mixture was pressure filtered through a 1μm filter pad and the resulting Et₃N · HCl salt cake was washed with three 50 ml portions of toluene. The combined filtrate and toluene extract of the salt cake were vacuum stripped to 100° C/33 mbar pressure to remove toluene, excess triethylamine and any other low boiling components. ¹³C, and ²⁹Si NMR indicate the product structure is

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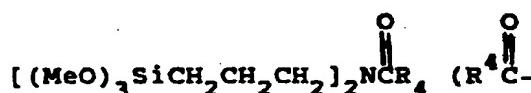


linseed acid chloride derivative).

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B.) In much the same equipment setup as described in A 85.3 g (0.25 moles) of $[(\text{MeO})_3\text{Si}(\text{CH}_2)_3]_2\text{NH}$ was stirred at 50° C while 37.11 g (0.125 moles) of linseed acid chloride was slowly added through a dropping funnel. An exotherm resulted throughout the addition and external cooling was used to control the reaction temperature between 50° and 60° C. The reaction mixture analyzed for 0.98 meq/gm chloride ion [96% of theoretical]. ¹³C and ²⁹Si, NMR indicate an equimolar mixture of

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a linseed acid chloride derivative) and $[(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2]_2\text{NH} \cdot \text{HCl}$.

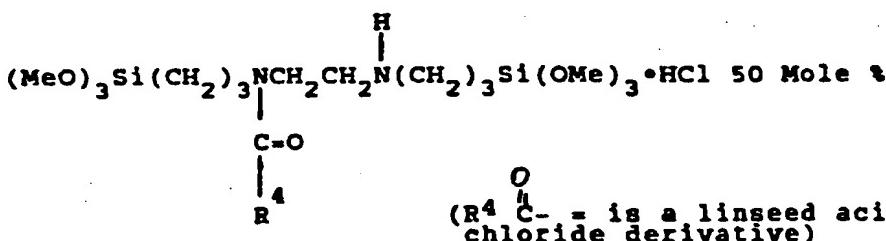
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C.) In the same equipment setup described in A 76.8 g (0.2 moles) of $[(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2]_2$ dissolved in 106.7 g (3.33 moles) of methanol was charged. The homogeneous mixture was stirred at room temperature and 29.7 g (0.10 moles) of linseed acid chloride was slowly added. An exotherm resulted throughout the addition and air cooling was used to control the reaction temperature between 50° and 60° C. The reaction mixture was heated to reflux methanol for one hour, cooled and analyzed for chloride ion [98.3% of theoretical]. The product mixture at 50 wt.% active in methanol, had a calculated average composition:

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D.) In much the same manner as described in C, 76.8 g (0.2 moles) of $[(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2]_2$ dissolved in 136.4 g (4.26 moles) of methanol was reacted with 59.4 g (0.20 moles) of linseed acid chloride. The resulting product, at 50 wt. % active in methanol, has a calculated average composition:

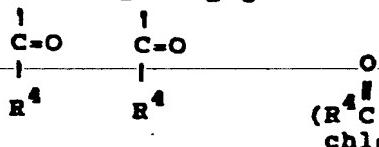
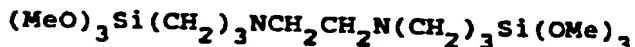


(R⁴C = is a linseed acid
chloride derivative)

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E.) In much the same manner as described in A 76.8 g (0.2 moles) of [(MeO)₃SiCH₂CH₂CH₂NHCH₂]₂, 50.6 g (0.5 moles) of triethylamine and 250 g of toluene was reacted with 118.7 g (0.4 moles) of linseed acid chloride to give the corresponding di("fatty" ethenoid acylamino)organo-bis-silane

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F.) In much the same manner described for C 265.4 g (1.0 mole) of NH₂CH₂CH₂NHCH₂CH₂NH(CH₂)₃Si(OMe)₃ dissolved in 562.4 g of methanol was reacted with 297 g (1.0 moles) of linseed acid chloride to produce the corresponding "fatty" ethenoid acylamino hydrochloride derivative with the average composition:

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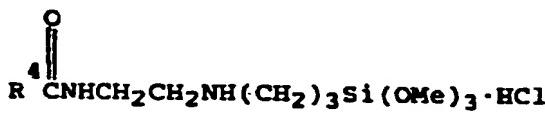


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where R⁴ is a linseed acid chloride derivative.

G.) In much the same manner described in C 222.1 g (1.0 moles) of NH₂CH₂CH₂NH(CH₂)₃Si(OMe)₃, dissolved in 519.1 g , of methanol, was reacted with 297 g (1.0 moles) of linseed acid chloride to produce the corresponding "fatty" ethenoid acylamino hydrochloride derivative with the average composition:

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 R⁴C is a linseed acid chloride derivative.

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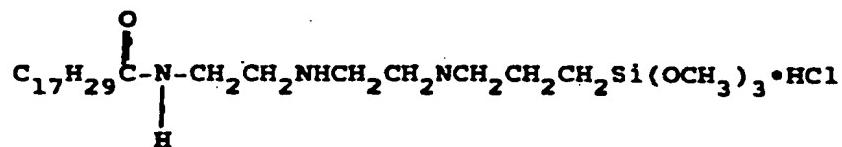
Example 1

To 98.1 parts water are added 0.4 parts of the "fatty" ethenoid acylamino organosilicon compound that is illustrated by the formula; C₁₇H₂₉CONHCH₂CH₂NHCH₂CH₂NHCH₂CH₂Si(OCH₃)₃ · HCl which is dissolved in methanol (50 weight percent). After the pH is adjusted to 11.52, 1.5 parts of aqueous emulsion of polyethylene that is 20% solids by weight is added with stirring at room temperature. The preparation of the

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polyethylene emulsion is disclosed in U.S. - A - 2,995,533.

The test results for the aqueous mixture of 0.2 weight percent



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and 0.3 weight percent solid polyethylene are given in Table II, Compound 1. Also shown in Table II are the commercial coatings and representative mixtures of 0.2 wt. percent acylaminosilanes, which do not belong to the "fatty" ethenoid acylaminosilicon compounds and 0.3 weight percent polyethylene.

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	1. The composition of the glass coating dissolved in water at pH 11.5	
X.	0.2 wt% $\text{C}_{17}\text{H}_{29}\text{C}(\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
A. Two step coating:	1. SnCl_2 sprayed.	2. 0.2 wt% polyethylene sprayed.
B.	0.2 wt% $\text{CH}_3\text{CNHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
C.	0.2 wt% $\text{CH}_3\text{CH}_2\text{CNHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
D.	0.2 wt% $\text{CH}_3\text{CH}_2\text{CH}_2\text{CNHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{NHICH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
E.	0.2 wt% $\text{CH}_3(\text{CH}_2)_4\text{CHN}(\text{CH}_2\text{CH}_2\text{NH})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
F.	0.2 wt% $\text{CH}_3\text{CH}_2\text{C}(\text{CNH}(\text{CH}_2\text{CH}_2\text{NH}))_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
G.	0.2 wt% $\text{CH}_2\text{C}(\text{CNH}(\text{CH}_2\text{CH}_2\text{NH}))_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0
H.	0.2 wt% $\text{HOCH}_2\text{CH}_2\text{C}(\text{NH}(\text{CH}_2\text{CH}_2\text{NH}))_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3\text{HCl}$ + 0.3 wt% polyethylene.	0

Bottle Coating Procedure

Test bottles are washed with acetone and heated in an oven to 565 °C for at least 4 hours to clean the glass surface, and then cooled to 177 °C. The bottles are then removed from the oven and immediately suspended from the shaft of an electric motor that is rotating at 50 rpm and are sprayed with the aqueous emulsion of the "fatty" ethenoid acylaminoorganosilicon compound and the polyethylene for 3 revolutions. A Devilbiss spray gun, Model #EGA-502 set for a fan pattern and siphon feed using 1.38 bar (20 psi) air pressure is used. The distance between the spray gun nozzle and the glass bottle is 457 mm (18 in). This spraying technique deposits approximately 0.037 g/cm² of the aqueous emulsion onto the glass surface. The coating quickly dries to form a clear, colorless film. The bottle is then removed and allowed to cool to room temperature before the bottles are tested.

Testing Procedures

1.) Scratch Test

Scratch resistance is measured on a laboratory scale static load tester. The device slides the surfaces

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of two bottles together at 45° under constant load. Load settings can be varied from 4.5 to 45 kg (10 to 100 pounds). The bottles pass at a particular load setting if no nicks are seen in the area of the test. Bottles are tested both wet and dry. In the wet test, the bottles are sprayed with a fine mist of water just prior to the test.

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2.) Lubricity Test

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Lubricity is expressed in terms of slip angle. Slip angle is measured on a motorized tilting table (manufactured by the American Glass Research Corporation). Three coated bottles are arranged in a pyramid on their sides on the table. The 2 bottom bottles are held in place and the third allowed to move. The table is tilted at a slow constant rate until the top bottle slips approximately 6.35 µm (1/4"). The angle at the point of slippage between the plane of the bottom of the 2 bottles and the horizontal is measured and recorded as the slip angle.

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3.) Label Adhesion

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The test method for determining label adhesion is performed in accordance with ASTM method D-3359-58. The labels are first coated with an adhesive - 51 to 76 µm at room temperature. The application is done by means of a wet film knife (127 µm wet). The bottles, affixed with labels, are heated at 60 °C for 20 minutes. After cooling to room temperature, a crosscut of 6.35 mm is made at an angle of 90° on the label. The grid area is examined to determine the extent of label adhesion as follows:

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- 0 (less than 50% of label remains on bottom after crosscut)
- 1 (~50% of label remains on bottle after crosscut)
- 2 (75% of label remains on bottle after crosscut)
- 3 (90% of label remains on bottle after crosscut)
- 4 (95% of label remains on bottle after crosscut)
- 5 (100% of label remains on bottle after crosscut)

A total of three crosscuts are made at random areas on the label with the average classification reported.

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4.) Aqueous Caustic Wash

The aqueous caustic wash consists of submerging a bottle into 70 °C, 5% by weight sodium hydroxide solution for 30 minutes, and then thoroughly rinsed with distilled water.

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5.) Appearance

A qualitative judgment of the coating's appearance is made by shining a bright light on the bottle in a dark room.

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Examples 2 to 10

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The coating compositions Nos. 2 to 10 are made, applied and tested as described above. Although the dry scratch resistance after caustic wash for coating compositions Nos. 2 to 10, (Table III) are less than for the first coating in Table II, the adhesion of common adhesives (casein, Vinyl Dex™, polyvinyl acetate and jelly gum) is considerably better, especially for coating No. 6 and 9 (Table III).

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1 Coating compositions 2-10 are Composed of an Aqueous Emulsion of 0.3 wt% Polyethylene and 0.2 wt% "Patty" Ethenoid Acylaminoorganosilicon Compounds with the structures 2-10.

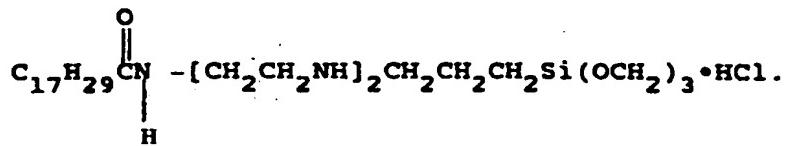
<u>Coating No.</u>	<u>Polyamine</u>	<u>Functional groups (moles/mole of polyamine)</u>			
		[R ⁴ C-]	[C ₃ H ₆ Si(OCH ₃) ₃]	[HCl]	[H]
2	NH ₂ CH ₂ CH ₂ NH ₂	1	1	1	0
3	NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂	1.4	1.2	1.2	0.4
4	NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂	1.2	1.6	1.6	0.2
5	NH ₂ (CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	2.0	1.0	1.0	1.0
6	NH ₂ (CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	2.0	1.4	1.4	0.6
7	NH ₂ (CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	2.0	1.7	1.7	0.3
8	NH ₂ (CH ₂ CH ₂ NH) ₃ CH ₂ CH ₂ NH ₂	2.0	1.0	1.0	2.0
9	NH ₂ (CH ₂ CH ₂ NH) ₃ CH ₂ CH ₂ NH ₂	2.0	1.7	1.7	1.3
10	NH ₂ (CH ₂ CH ₂ NH) ₃ CH ₂ CH ₂ NH ₂	2.0	2.5	2.5	0.5

R⁴C- is a linseed acid chloride derivative.

Examples 11-13

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To 98 parts water are added varying amounts of



After the pH is adjusted to 11.5, 1.5 parts of an aqueous emulsion of polyethylene that is 20% solids by weight is added with stirring at room temperature. The preparation of the polyethylene emulsion is disclosed in U.S. - A - . 2,995.533. The coating and testing procedures are described in Example 1. Data are given in Table IV.

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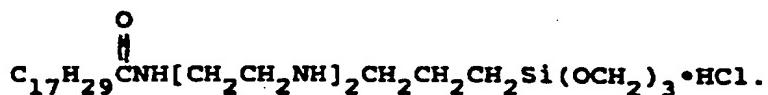
Examples 14-19

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To 98 parts water is added 0.5 parts

Table IV

<u>Coating No.</u>	<u>Concn of silane (wt. %)</u>	<u>Appearance</u>	<u>Scratch (dry/wet)</u>	<u>Lubricity (dry/wet)</u>	<u>Availability Casein Vinyl dextm</u>	<u>Polyvinyl Acetate</u>
11	0.1	good	36	/31.5	4.5/40.5	0
12	0.2	good	45	/40.5	4.5/40.5	0
13	0.5	good	31.5	/31.5	12.0/15.0	0



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After the pH is adjusted to 11.5, 1.5 parts of an aqueous emulsion of polyethylene that is 20% solids by weight is added with stirring at room temperature. The preparation of the polyethylene emulsion is disclosed in U.S. - A - 2,995,533. The coating and testing procedures are described in Example 1, except that the 10 temperature of the glass surface is varied during the spraying operation. Data are given in Table V.

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Table V

<u>Temperature of glass surface °C (°F)</u>	<u>Scratch (dry/ kg)</u>	<u>Lubricity (dry)</u>	<u>Labelability casein Vinylidex™</u>
15 (75)	22.5	16°	0
38 (100)	31.5	13°	0
93 (200)	31.5	14°	1
121 (250)	31.5	14°	2
149 (300)	31.5	14°	4
176 (350)	31.5	14°	2

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Examples 20-23

Into 99 parts water is added 1 part fatty ethenoid acylaminoorganosilicon compound and the pH is adjusted to 7 (Solution A).

5 Into 98.5 parts water is added 1.5 parts aqueous emulsion of 20% solids polyethylene. The preparation of the polyethylene emulsion is disclosed in U.S. - A - 2,995,533 (Solution B).

Bottle Coating Procedure

- 10 Test bottles are washed with acetone and heated in an oven to 565°C for at least 4 hours to clean the glass surface, and then cooled to 177°C. The bottles are then removed from the oven and immediately suspended from the shaft of an electric motor that is rotating at 50 rpm and are sprayed with Solution A for 3 revolutions. A Devilbiss spray gun, Model #EGA-502, set for a fan pattern and siphon feed using 1.38 bar (20 psi) air pressure is used. The distance between the spray gun nozzle and the glass bottle is 45.7 mm
15 (18 in). Within 1 minute, the glass bottles are sprayed with Solution B under similar conditions as that used for spraying Solution A. The bottle are allowed to cool and then they were tested according to the procedures outlined in Example 1. Data are given in Table VI.

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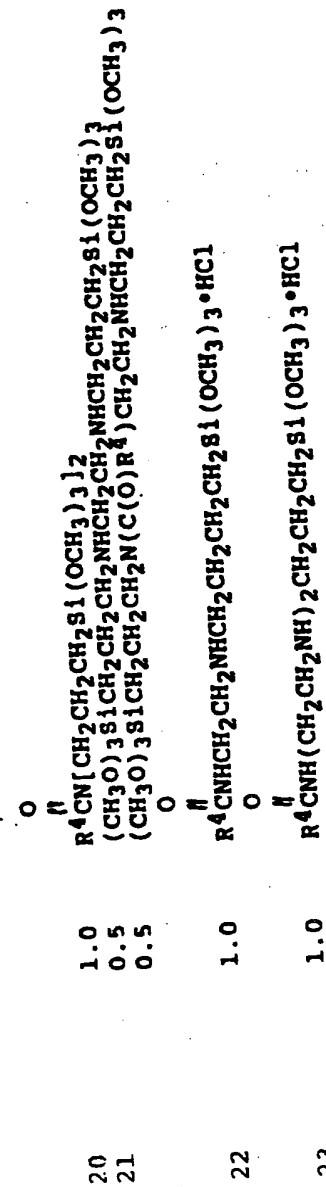
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<u>Coating¹</u>	<u>Appearance</u>	<u>scratch (dry/wet) kg</u>	<u>Lubricity (dry/wet)</u>	<u>LabelabilityTM Casein Vinylidex</u>	<u>Polyvinyl Acetate</u>
20	good	45/18	(13°/16°)	1	0
21	good	45/22.5	(12°/13°)	3	0
22	good	45/31.5	(13°/16°)	--	--
23	good	36/27	(10°/15°)	--	--

1 The composition of solution A.

<u>Compound in Coating No.</u>	<u>Concn. of silane (wt. %)</u>	<u>structure</u>
20	1.0	$\text{R}^4\text{CN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3)_2$
21	0.5	$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
	0.5	$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{C}(\text{O})\text{R}^4)\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$
	0	O



O
 $\text{(R}^4\text{C-}$ is a linseed acid chloride derivative).

Examples 24-31 (Comparative Examples)

Into 99 parts water is added 1 part of the fatty ethenoid acylaminoorganosilicon compound. The bottle is coated and tested as described in Example 1.

TABLE VII

TEST DATA BEFORE CAUSTIC WASH²

<u>Coating¹</u>	<u>Appearance</u>	<u>Lubricity (dry/wet)</u>	<u>Scratch (dry/wet) kg</u>	<u>Casein</u>	<u>Vinyl dex™</u>	<u>Polyvinyl Acetate⁶</u>
24	good	12°/11°	27 /27	2	0	2
25	good	15°/14°	18 /18	4	0	1
26	good	9°/8°	27 /31.5	2	0	1
27	good	12°/11°	18 /27	3	0	1
28	good	10°/9°	18 /27	2	0	2
29	good	16°/14°	18 /31.5	2	0	1
30	good	14°/13°	18 /18	2	0	2
31	good	10°/8°	31.5/18	4	1	2
			22.5/31.5	0		0

TEST DATA AFTER CAUSTIC WASH²

24	good	18°/14°	4.5/-
25	good	23°/13°	9 /-
26	good	18°/12°	18 /-
27	good	19°/11°	9 /-
28	good	16°/13°	4.5/-
29	good	21°/21°	13.5/-
30	good	23°/18°	18 /-
31	good	14°/11°	4.5/-

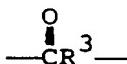


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wherein

R and R¹ are individually selected from alkylene groups containing from 2 to 6 carbon atoms; arylene groups containing from 6 to 12 carbon atoms; alkyl substituted arylene groups containing from 7 to 20 carbon atoms; and

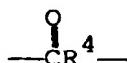
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R² wherein R³ is a alkylene group containing from 2 to 6 carbon atoms; is an alkyl or aryl group containing from 1 to 10 carbon atoms or hydrogen; W is either hydrogen or

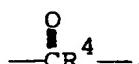
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Y wherein R⁴ is a hydrocarbon group containing from 8 to 24 carbon atoms and containing at least one double bond; is selected from hydrogen,

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R² and -R⁵Si(OR⁶)_{3-a}(R⁷)_a wherein R⁵ is an alkylene group containing from 2 to 6 carbon atoms;

R⁶ and R⁷ are individually an alkyl or aryl group containing from 1 to 6 carbon atoms; and R⁶ may also be a silicon containing moiety wherein the oxygen atom is directly bonded to the silicon atom of the R⁶ silicon containing moiety;

40

X is selected from a halogen atom; a hydroxy group, an ester group and an anhydride group and

a has a value of 0,1 or 2;

b has a value of 0,1 or 2;

c has a value of 0 or 1;

x and y have values such that x + y = 1 to 30 with the proviso that x is at least 1;

z is 0 or 1;

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w has a value equal to from 0 to the sum of x+y+z provided that w does not exceed the total nitrogen atom in free amine form; with the proviso that at least 1 Y is -R⁵Si(OR⁶)_{3-a}(R⁷)_a and at least 1 other Y is

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a dispersing agent and a fatty acid and optionally a polymer.

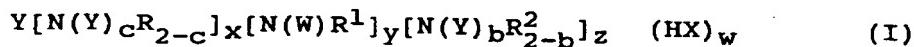
55 2. The coating composition of claim 1, wherein R and R¹ in the fatty ethenoid acylaminoorganosilicon compound are alkylene radicals.

3. The coating composition of claims 1 to 2 wherein R and R¹ are ethylene or propylene.

4. The coating composition of claims 1 to 3 wherein R² in the fatty ethenoid acylaminoorganosilicon compound is methyl or hydrogen.
5. The coating composition of claims 1 to 4 wherein R⁵ in the fatty ethenoid acylaminoorganosilicon compound is propylene,
6. The coating composition of claims 1 to 5 wherein R⁶ and R⁷ in the fatty ethenoid acylaminoorganosilicon compound are methyl or ethyl.
10. The coating compositions of claims 1 to 6 wherein in the fatty ethenoid acylaminoorganosilicon compound a = 0 or 1, b = 0 or 1, c = 1, x = 1 to 4, y = 0 to 3 and z = 0 or 1.
15. The coating composition of claims 1 to 7 wherein the dispersing agent is water or an organic solvent.
20. The coating composition of claims 1 to 8 wherein the polymer is selected from polyolefins, polyethers and polyepoxides.
25. The coating composition of claims 1 to 9 wherein the fatty acid contains from 8 to 18 carbon atoms and is preferably stearic acid, oleic acid and linolenic acid.
30. The coating composition of claims 1 to 10 wherein the fatty acid comprises from 0.1 to 50 weight percent of the composition.
35. The coating composition of claims 1 to 11 comprising 0.01 to 20 weight percent of the fatty ethenoid acylaminoorganosilicon compounds, 0.01 to 50 weight percent polymer and/or fatty acid and the remainder dispersing agent.
40. The use of the fatty ethenoid acylaminoorganosilicon compound as defined in claim 1 together with a dispersing agent and a polymer and/or a fatty acid for enhancing the surface properties of glass articles with the exception of glass fibers.

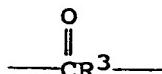
Revendications

35. 1. Composition de revêtement pour le revêtement d'articles en verre, comprenant un composé d'acylamino-organosilicium éthénoid gras représenté par la formule :



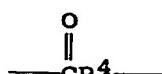
40. dans laquelle

R et R¹ sont choisis individuellement entre des groupes alkylène contenant 2 à 6 atomes de carbone ; des groupes arylène contenant 6 à 12 atomes de carbone ; des groupes arylène à substituant alkyle contenant 7 à 20 atomes de carbone ; et des groupes



50. dans lesquels R³ représente un groupe alkylène contenant 2 à 6 atomes de carbone ;

R² représente un groupe alkyle ou aryle contenant 1 à 10 atomes de carbone ou l'hydrogène ;
W représente l'hydrogène ou un groupe

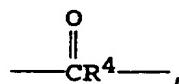


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dans lequel R⁴ représente un groupe hydrocarboné contenant 8 à 24 atomes de carbone et contenant au moins une double liaison ;

Y est choisi entre l'hydrogène, des groupes

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R² et -R⁵Si(OR⁶)_{3-a}(R⁷)_a

dans lesquels R⁵ représente un groupe alkylène contenant 2 à 6 atomes de carbone ; R⁶ et R⁷ représentent individuellement un groupe alkyle ou aryle contenant 1 à 6 atomes de carbone ; et R⁶ peut représenter également un groupement contenant du silicium dans lequel l'atome d'oxygène est lié directement à l'atome de silicium du groupement R⁶ contenant du silicium ;

X est choisi entre un atome d'halogène, un groupe hydroxy, un groupe ester et un groupe anhydride ; et a a la valeur 0, 1 ou 2 ;

b a la valeur 0, 1 ou 2 ;

c a la valeur 0 ou 1 ;

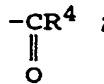
x et y ont des valeurs choisies de sorte que la somme x + y soit égale une valeur de 1 à 30, sous réserve que x soit au moins égal à 1 ;

z a la valeur 0 ou 1 ;

w a une valeur de 0 à la somme x+y+z, sous réserve que w n'excède pas le nombre total d'atomes d'azote dans la forme amine libre ; sous réserve qu'au moins un groupe Y représente un groupe -R⁵Si(OR⁶)_{3-a}(R⁷)_a et au moins un autre groupe Y représente un groupe

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un dispersant, un acide gras et, facultativement, un polymère.

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2. Composition de revêtement suivant la revendication 1, dans laquelle R et R¹, dans le composé d'acylamino-organosilicium éthénoidé gras, représentent des radicaux alkylène.
3. Composition de revêtement suivant la revendication 1 ou 2, dans laquelle R et R¹ représentent des radicaux éthylène ou propylène.
4. Composition de revêtement suivant les revendications 1 à 3, dans laquelle R², dans le composé d'acylamino-organosilicium éthénoidé gras, représente un groupe méthyle ou l'hydrogène.
- 45 5. Composition de revêtement suivant les revendications 1 à 4, dans laquelle R⁵, dans le composé d'acylamino-organosilicium éthénoidé gras, représente un groupe propylène.
6. Composition de revêtement suivant les revendications 1 à 5, dans laquelle R⁶ et R⁷, dans le composé d'acylamino-organosilicium éthénoidé gras, représentent des groupes méthyle ou éthyle.
- 50 7. Composition de revêtement suivant les revendications 1 à 6, dans laquelle, dans le composé d'acylamino-organosilicium éthénoidé gras, a est égal à 0 ou 1, b est égal à 0 ou 1, c est égal à 1, x a une valeur de 1 à 4, y est égal à une valeur de 0 à 3 et z est égal à 0 ou 1.
- 55 8. Composition de revêtement suivant les revendications 1 à 7, dans laquelle le dispersant consiste en eau ou en un solvant organique.
9. Composition de revêtement suivant les revendications 1 à 8, dans laquelle le polymère est choisi entre

des polyoléfines, des polyéthers et des polyépoxydes.

10. Composition de revêtement suivant les revendications 1 à 9, dans laquelle l'acide gras contient 8 à 18 atomes de carbone et consiste de préférence en acide stéarique, en acide oléique ou en acide linolénique.
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11. Composition de revêtement suivant les revendications 1 à 10, dans laquelle l'acide gras représente 0,1 à 50 % en poids de la composition.
- 10 12. Composition de revêtement suivant les revendications 1 à 11, comprenant 0,01 à 20 % en poids du composé d'acylamino-organosilicium éthénoidé gras, 0,01 à 50 % en poids de polymère et/ou d'acide gras, le reste consistant en le dispersant.
- 15 13. Utilisation du composé d'acylaminoorganosilicium éthénoidé gras suivant la revendication 1, en association avec un dispersant et un polymère et/ou un acide gras pour accroître les propriétés de surface d'articles en verre, à l'exception des fibres de verre.

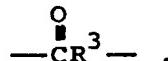
Patentansprüche

- 20 1. Beschichtungsmassen zum Beschichten von Glaserzeugnissen, die eine Ethenoid-acylaminoorganosilicium-Fett-Verbindung, wiedergegeben durch die Formel



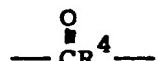
in der:

30 R und R¹ jeweils aus Alkylengruppen mit 2 bis 6 Kohlenstoffatomen, Arylengruppen mit 6 bis 12 Kohlenstoffatomen, Alkyl-substituierten Arylengruppen mit 7 bis 20 Kohlenstoffatomen und



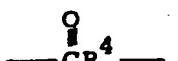
worin R³ eine Alkylengruppe mit 2 bis 6 Kohlenstoffatomen bedeutet, ausgewählt sind;

40 R² eine Alkyl- oder Arylgruppe mit 1 bis 10 Kohlenstoffatomen oder Wasserstoff ist; W entweder Wasserstoff oder



worin R⁴ eine Kohlenwasserstoffgruppe mit 8 bis 24 Kohlenstoffatomen, die mindestens eine Doppelbindung enthält, ist; aus Wasserstoff,

50 Y



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R² und -R⁵Si(OR⁶)_{3-a}(R⁷)_a, worin R⁵ eine Alkylengruppe mit 2 bis 6 Kohlenstoffatomen bedeutet, ausgewählt ist;

R⁶ und R⁷ jeweils eine Alkyl- oder Arylgruppe mit 1 bis 6 Kohlenstoffatomen bedeuten, und R⁶

auch ein Silicium-enthaltender Molekülteil sein kann, in dem das Sauerstoffatom direkt an das Siliciumatom des R⁶ Silicium-enthaltenden Molekülteils gebunden ist;

X ein Halogenatom, eine Hydroxygruppe, eine Estergruppe oder eine Anhydridgruppe bedeutet und

5 a einen Wert von 0, 1 oder 2 besitzt,

b einen Wert von 0, 1 oder 2 besitzt,

c einen Wert von 0 oder 1 besitzt,

x und y solche Werte haben, daß x + y = 1 bis 30, mit der Maßgabe, daß x mindestens 1 ist,

10 z 0 oder 1 ist,

w einen Wert im Bereich von 0 bis zur Summe von x+y+z hat, mit der Maßgabe, daß w nicht die Gesamtzahl Stickstoffatome in freier Aminform übersteigt; mit der Maßgabe, daß mindestens ein Y -R⁵Si(OR⁶)_{3-a}(R⁷)_a ist und mindestens ein anderes Y

15



20

ist;

ein Dispergiermittel und eine Fettsäure und gegebenenfalls ein Polymer enthalten.

2. Beschichtungsmasse nach Anspruch 1, worin R und R¹ in der Ethenoid-acylaminoorganosilicium-Fett-Verbindung Alkylengruppen sind.
- 25 3. Beschichtungsmasse nach Anspruch 1 oder 2, worin R und R¹ für Ethylen oder Propylen stehen.
4. Beschichtungsmasse nach den Ansprüchen 1 oder 3, worin R² in der Ethenoid-acylaminoorganosilicium-Fett-Verbindung Methyl oder Wasserstoff bedeutet.
- 30 5. Beschichtungsmasse nach den Ansprüchen 1 bis 4, worin R⁵ in der Ethenoid-acylaminoorganosilicium-Fett-Verbindung Propylen bedeutet.
6. Beschichtungsmasse nach den Ansprüchen 1 bis 5, worin R⁶ und R⁷ in der Ethenoid-acylaminoorganosilicium-Fett-Verbindung Methyl oder Ethyl bedeuten.
- 35 7. Beschichtungsmassen nach den Ansprüchen 1 bis 6, worin in der Ethenoid-acylaminoorganosilicium-Fett-Verbindung a = 0 oder 1, b = 0 oder 1, c = 1, x = 1 bis 4, y = 0 bis 3 und z = 0 oder 1 ist.
- 40 8. Beschichtungsmasse nach den Ansprüchen 1 bis 7, worin das Dispergiermittel Wasser oder ein organisches Lösungsmittel ist.
9. Beschichtungsmasse nach den Ansprüchen 1 bis 8, worin das Polymer aus Polyolefinen, Polyethern und Polyepoxiden ausgewählt ist.
- 45 10. Beschichtungsmasse nach den Ansprüchen 1 bis 9, worin die Fettsäure 8 bis 18 Kohlenstoffatome enthält und vorzugsweise Stearinsäure, Ölsäure und Linolensäure ist.
11. Beschichtungsmasse nach den Ansprüchen 1 bis 10, worin die Fettsäure 0,1 bis 50 Gew.-% der Masse ausmacht.
- 50 12. Beschichtungsmasse nach den Ansprüchen 1 bis 11, die 0,01 bis 20 Gew.-% der Ethenoid-acylaminoorganosilicium-Fett-Verbindung, 0,01 bis 50 Gew.-% Polymer und/oder Fettsäure und als Rest Dispergiermittel enthält.
- 55 13. Verwendung der in Anspruch 1 definierten Ethenoid-acylaminoorganosilicium-Fett-Verbindung zusammen mit einem Dispergiermittel und einem Polymeren und/oder einer Fettsäure zur Verbesserung der Oberflächeneigenschaften von Glaserzeugnissen, ausgenommen Glasfasern.

